

II. "On the Absorption-Spectra of Metals volatilized by the Oxyhydrogen Flame." By J. NORMAN LOCKYER, F.R.S., and W. CHANDLER ROBERTS, Chemist of the Mint. Received February 4, 1875.

The researches which have recently been published on the absorption-spectra of various metals, first by Roscoe and Schuster and subsequently by one of us\*, establish beyond all question the facts that—

I. In addition to the well-known line-spectra, chaunelled-space spectra are produced by the vapours of certain metals; and,

II. Such spectra are produced by vapours which are competent to give at other times, not only line-spectra, but continuous spectra in the blue, or blue and red.

As the temperature employed for the volatilization of the metals in the experiments to which we have referred did not exceed bright redness, or that at which cast iron readily melts, the range of metals examined was necessarily limited. We have therefore considered it desirable to extend these observations to the less fusible metals, as well as to ascertain whether the spectra of those which were volatilized at the lower temperature would be modified by the application of a greater degree of heat. For this purpose we have employed the flame of an oxyhydrogen blowpipe. This instrument, devised by Sainte-Claire Deville and Debray†, renders it possible to attain high temperatures with great facility, and Stas has already employed their method in the distillation of silver‡. The lime still arranged by him has been modified in that about to be described, in order that the metallic vapour might be conducted into a lime tube or tunnel heated to whiteness, so placed that a beam from an electric lamp could readily traverse it.

#### *Description of the Apparatus and method of Manipulation.*

The apparatus employed is shown in the figure, in which A is the block of lime § divided horizontally by a plane through the axis of the tube (B B'), this tube being 16 centims. long and 30 millims. diameter. The receptacle (C) communicates with the centre of B B', and is open at the upper surface of the lime block, in order to admit of the introduction of the oxyhydrogen blowpipe (D), which is provided with a thick nozzle of platinum 20 millims. in diameter. The ends of the tunnel in the lime were closed by glass plates held on by a suitable clip. Small

\* Proc. Roy. Soc. vol. xxii, pp. 362 and 371 respectively.

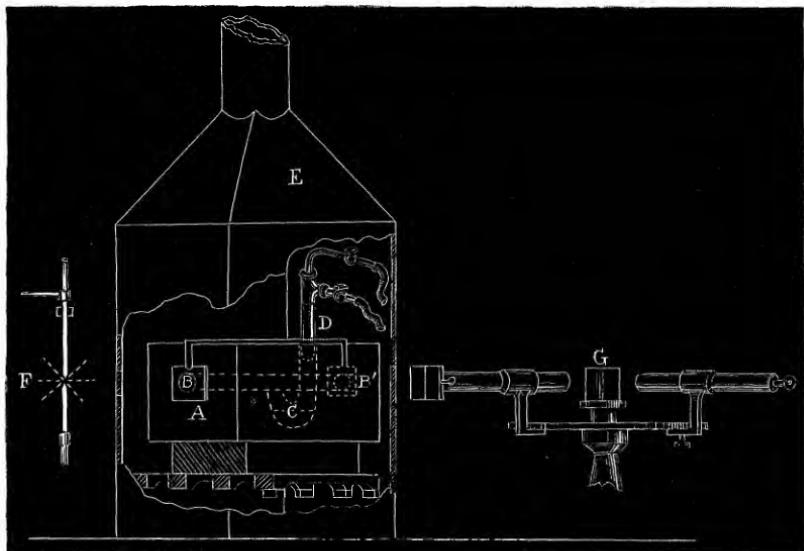
† Ann. de Chimie et de Physique, tom. lvi. p. 413.

‡ Stas, 'Sur les lois des proportions Chimiques,' p. 56.

§ We are indebted to the well-known metallurgist, Mr. J. S. Sellon, of the firm of Johnson and Matthey, for a pure variety of limestone from which the blocks were prepared, and it answered its purpose admirably.

lateral orifices were cut in the lime for the insertion of tobacco-pipe stems, through which a stream of hydrogen could be passed into the tube and receptacle.

An electric lamp (F), in connexion with a 30-cell Bunsen's battery,



was placed opposite one end of the tube, and a spectroscope (G) opposite the other. This last instrument was by Desaga, of Heidelberg, and its single prism, the angle of which was  $60^\circ$ , was capable of distinctly separating the D lines, at the same time that it enabled us to see the whole spectrum in a single field of view, an essential point in such inquiries. The magnifying-power of the telescope was 7.5 linear.

Some preliminary experiments indicated the advisability of increasing the length of the column of vapour. To effect this, a tube 30 centims. long was made in a fresh block of lime, the cavity being arranged as before; in each end a short accurately fitting iron tube, luted with a mixture of graphite and fireclay, was inserted; and the total length of the column thus became 60 centims.

The lime block (C) with its fittings was then placed in the charcoal-furnace (E), by means of which the whole could be raised to a high temperature. As soon as the block was heated to bright redness, the metal, the vapour of which was to be examined, was introduced into the cavity (C), and the flame of the oxyhydrogen blowpipe (D) was allowed to play on its upper surface, care being taken to employ an excess of hydrogen. In almost every case the metal experimented on was rapidly volatilized (the exceptions being gold and palladium). The central portion of the

lime block was raised to a white heat by the action of the blowpipe. As the glass plates rapidly became clouded by the condensation of the metallic vapours, it was necessary to adopt an arrangement by which they could be easily replaced. We may state that, among the precautions which we adopted in order to assure ourselves that oxides were not present to disturb the accuracy of the results, one of the glass plates was removed at the conclusion of each experiment, and the presence of an excess of hydrogen conclusively proved by igniting it at the open end.

We were enabled at any time, by modifying the conditions of the gas-supply, to introduce the spectrum of the oxyhydrogen flame. It may further be stated that, with few exceptions, the metals were previously melted in a stream of hydrogen and enclosed, until experimented on, in sealed glass tubes. We ascertained that the effect of oxides, and of the metallic rain due to condensation, was to produce a general absorption obviously different from the special effects of absorption which we now proceed to record.

#### DETAILS OF THE EXPERIMENTS.

##### *Silver.*

Fifty grammes of pure metal were placed in the cavity (C), and this amount produced a continuous supply of vapour for about 10 minutes.

With the smaller thickness given by the first lime block, and with a less powerful blast, the spectrum of silver consisted of an absorption in the blue which at times extended almost to the green.

With the elongated tube and a stronger blast an exquisite channelled-space absorption was observed, the channels being far enough apart to render them very conspicuous in the field of view; at the same time there was continuous absorption in the blue. It was specially observed that there was no absorption in the red.

It may be interesting to note that the vapour of silver when condensed into fine particles, escaping into an atmosphere of hydrogen, is blue by reflected light.

##### *Copper.*

With the greatest thickness only a continuous absorption in the blue could be obtained.

##### *Sodium.*

Only the *dark D* line was observed, no traces of channelled-space absorption being visible.

##### *Calcium.*

We operated upon a small piece of metal prepared by the late Dr. Matthiessen, but no result was obtained.

*Aluminium.*

When the temperature was so high that the spectrum of the flame was visible, an absorption was suspected in the violet; and the appearance did not change on one glass end being removed.

*Zinc.*

Many experiments were made on this metal; but there are several points connected with it which require further investigation, and we therefore reserve our remarks on the spectrum of zinc for a future occasion.

*Cadmium.*

Under both conditions of thickness the vapour of cadmium gave, in the blue only, an absorption which was very decided; an absorption in the red was also noticed which had not been observed in previous experiments when a low temperature was employed.

*Manganese.*

A small quantity of this metal was prepared with great care by Mr. Bayly, one of the assistant assayers, and it gave a distinct absorption in the red and blue, with evidences of a channelled-space spectrum. In a repetition of the experiment a more distinct channelled-space spectrum was observed.

*Iron.*

The metal employed had been obtained by electro-deposition in the manner suggested by Mr. Jacobi. Its vapour gave a slight continuous absorption in the blue.

*Cobalt*

also gave a slight continuous absorption in the blue, but less than in the case of iron.

*Nickel.*

This metal behaved in the same manner as cobalt, the absorption being about equal in amount.

*Chromium.*

The amount of metal volatilized was very small, but a fine channelled-space spectrum was observed.

*Tin.*

This metal caused a considerable absorption in the blue, but less in the red, no traces of a channelled-space spectrum being visible.

*Antimony.*

In results already published it is stated that at the low temperature antimony gives a channelled-space spectrum. In the present experi-

ments we observed merely absorption in the blue; and this is the only case in which the effects at a high temperature were inferior to those at a low temperature. As the purity of the metal first employed may be doubted, little reliance can be placed on these exceptional results.

#### *Bismuth.*

With the greatest thickness the absorption of bismuth is strikingly similar to that of iodine at a dull red heat. We have first a bank of continuous absorption in the blue with a sharp boundary on the less refrangible side, and then a channelled-space absorption throughout the entire green part of the spectrum reaching to D.

#### *Lead.*

This metal at first caused an absorption at both ends of the spectrum; shortly afterwards the whole spectrum was extinguished. As this is a readily oxidizable metal, special care was taken to prove that a large excess of hydrogen was present.

#### *Thallium.*

We are indebted to Mr. Crookes for a generous supply of this metal. The characteristic green line of thallium was observed *bright*, the light of the arc not being reversed; and it may be interesting to note that the vapour of this metal was incandescent five minutes after the withdrawal of the flame.

#### *Gold.*

A distinct absorption in the blue and red was observed, but there were certainly no traces of a channelled-space spectrum. The spectral lines due to the oxyhydrogen flame were very conspicuous. It may be noted that the amount of gold volatilized was only 0.01 oz.; but this quantity of metal was sufficient to produce an abundant supply of vapour.

#### *Palladium.*

This metal caused a distinct absorption in the blue, but no effect was noticed at the red end of the spectrum. There was no channelled-space spectrum, and the lines caused by the oxyhydrogen flame were barely visible.

#### *Selenium.*

With the greatest thickness employed a channelled-space spectrum was given by selenium.

#### *Iodine.*

It will be remembered that, according to the results already published by one of us, iodine vapour exhibits, at a low temperature, a channelled-space spectrum, and a bank of absorption in the violet. These later experiments showed that, at the more elevated temperature, this bank

was broken up and disappeared, leaving a continuous channelled-space spectrum.

These experiments, made at the Royal Mint, were often prolonged for many hours consecutively. They involved much furnace-work of a peculiarly trying nature; and we have much pleasure in acknowledging the assistance we received from Mr. Edward Rigg, one of the assistant assayers, who conducted many of the tedious manipulations with great skill and patience. We should also mention that the care exercised by Joseph Groves, senior fireman, in the preparation of the furnace and the lime-moulds, contributed in no small measure to the success of the experiments.

It appears to us that these experiments, conducted at the high temperature of the oxyhydrogen flame, go far to support the conclusions which were drawn from the experiments at a lower temperature. First, in passing from the liquid to the most perfect gaseous state, vapours are composed of molecules of different orders of complexity; and second, this complexity is diminished by the dissociating action of heat, each molecular simplification being marked by a distinctive spectrum. There is also an intimate connexion between the facility with which the final stage is reached, the group to which the element belongs, and the place which it occupies in the solar atmosphere.

III. "On the Liquation, Fusibility, and Density of certain Alloys of Silver and Copper." By W. CHANDLER ROBERTS, Chemist of the Mint. Communicated by Dr. PERCY, F.R.S. Received March 11, 1875.

(Abstract.)

The author states that the most remarkable physical property of silver-copper alloys is a molecular mobility, in virtue of which certain combinations of the constituents of a molten alloy become segregated from the mass, the homogeneous character of which is thereby destroyed. These irregularities of composition have long been known, and reference is made to them in the works of Lazarus Erckern (1650) and of Jars (1774). A very complete memoir was published in 1852 by Levol, who did much towards ascertaining the nature and defining the limits of this molecular mobility. He discovered the important fact that an alloy containing 71·89 per cent. of silver is uniform in composition. Its chemical formula ( $Ag_3 Cu_2$ ) and peculiar structure led him to conclude that all other alloys are mixtures of this, with excess of either metal.

The electric conductivity of these alloys was studied in 1860 by Matthiessen, who doubted the accuracy of Levol's theory, and viewed them as "mechanical mixtures of allotropic modifications of the two metals in each other."

